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Threshold switching effects in amorphous CuInSeS thin films

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Abstract : The switching effects in amorphous CuInSeS thin films have been investigated. The amorphous CuInSeS thin films were obtained by thermal evaporation of the polycrystalline materials under vacuum of about 10^{-6} Torr and with evaporation rate about 80 Å/ sec. The annealing of the films at different annealing temperature improves the switching characteristics and decreases the threshold voltage V_{th}. The threshold switching voltage and threshold activation energy E_t were found to decrease linearly with increasing annealing temperature and decreasing with thickness. Moreover, the threshold switching voltage increased exponentially with temperature.

Keywords : Amorphous semiconductor, CuInSeS thin films, threshold switching effects

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1. Introduction

In amorphous semiconductor films, electric breakdown effects have drawn particular attention since the discovery that electrical breakdown can be a regenerative and non-destructive process [1-6]. However, the breakdown mechanism is still unclear. Various models based on thermal and mixed electrothermal mechanisms have been proposed [3, 4, 7, 8]. Boer and Ovshinsky [8] have shown that the phenomenon of switching is limited by Joule heating of a current channel, which produces thermally stabilized high electric field effects close to the electrodes. These effects are responsible for starting the switching process.

A few studies on the electrical and optical properties of CuInSeS thin films have been reported [9-13]. However, there are no published studies, to our knowledge, on the switching phenomenon in CuInSeS thin films. The same author has studied the electrical and optical properties of CuInSeS thin films [14, 15].

This paper reports the results of a study of the switching properties of thermally evaporated CuInSeS thin films, which has led to the conclusion that the switching phenomenon is essentially thermal in nature.

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2. Experimental

The copper indium sulphoselenide was preparated by fusion method using spectroscopically pure Cu, In, Se and S (99.999 Mathey Chemical Lt) in the proper ratio [14]. A Leybold Univex 300 coating unit equipped with a quartz thickness monitor was used for thin films synthesis in a vacuum around 10^{-6} Torr. The thin films were evaporated onto polished pyrographite substrates at a rate of 80Å/sec by heating a fine – grained CuInSeS powder in a tungsten boat. The thickness of the produced films was also measured using an optical multiple – beam interferometer method.

The structure of CuInSeS in both powder and thin film forms were investigated by using X-ray diffractometer (Philips PW 1373) and a diffraction electron microscopy (DEM).

The compositional studies of CuInSeS in both powder and thin films were carried out by atomic absorption GBC 980 and Perkin Elmer (model 1100).

Current – voltage characteristics were measured in a two-electrodes cell through the CuInSeS films (current perpendicular to the film). The lower electrode, made out of copper, was in good contact with the pyrographite substrate. The upper electrode was a movable platinum wire of diameter ~ 200 μ m at its tip (the copper and the platinum electrodes give an ohomic contact all over the investigated range). This tip provided a good electrical contact with the upper film surface using a weak spring. The pressure exerted by the two electrodes on the film was kept constant throughout the measurements. A highly stabilized power supply, a sensitive voltmeter and an electrometer capable of measuring down to 10^{-11}A were used in measuring the I–V characteristics. A heater and a thermocouple were used for providing heat and measuring the temperature of the film during the experiment.

3. Results and discussion

The X-ray diffraction (XRD) as well as the diffraction electron microscope (DEM) studies, demonstrated the amorphous structure of the as-deposited (303 K) CuInSeS films. After annealing these films at different annealing temperatures (328, 353, 378, 398 and 423 K), no change of their amorphous structure has been observed and all these films retain the amorphous structure [15] as shown in Figure 1.

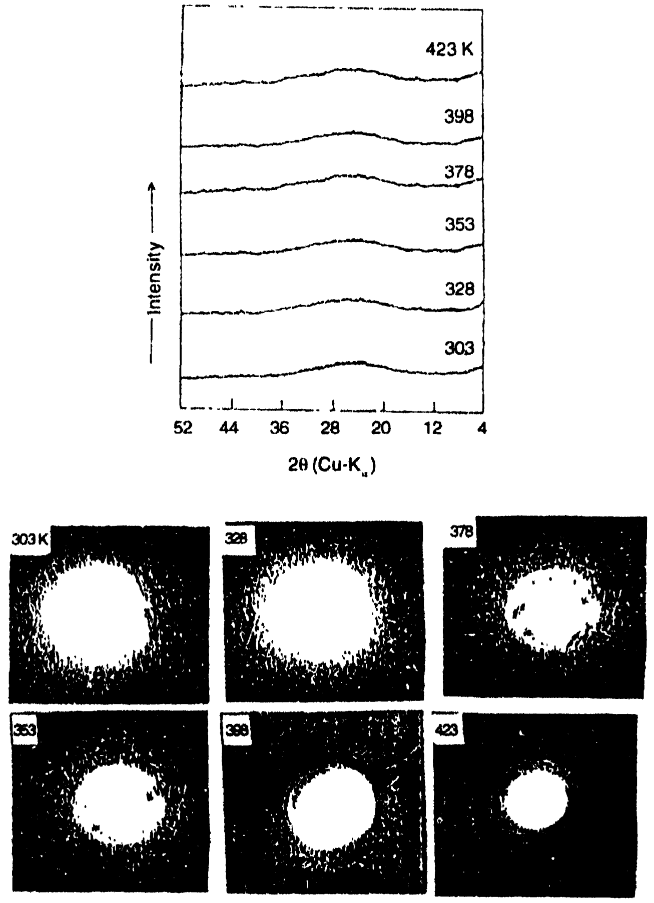

Figure 1. X-ray diffraction patterns (A) and electron diffraction patterns (B) of CuInSeS thin films as-deposited and annealed at different annealing temperatures.

The chemical composition analysis of CuInSeS in both powder and thin films form are reported in Table 1. It was found that these results confirm the stoichiometric composition of these films.

Table 1. Chemical analysis of CuInSeS, powder and thin films (as-deposited and annealed at 423 K).

Elements%	Powder	Thin films (as-deposited)	Thin films (annealed at 423 K)
Cu	22.028	22 031	21 998
In	39.620	39 606	39 604
Se	27.306	27.349	27.345
S	11.044	10.995	10 993

Room temperature static I–V characteristics for CuInSeS thin films of thickness 323 nm and 275 nm are shown in plot A and B of Figure 2 respectively. It is clear that the current is very small and that it increases on increasing the applied voltage {see part (oa) of the Figure 2–A}. This is called the 'off state'. This off

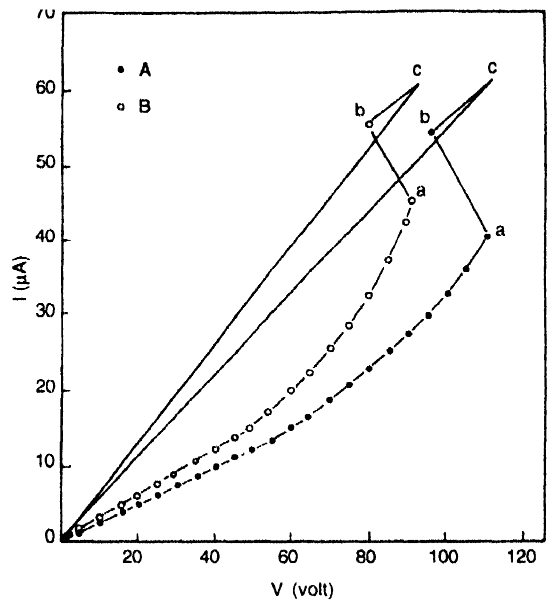

Figure 2. Current-voltage characteristics for CuInSeS thin films at 303 K of thickness (A) 323 nm and (B) 275 nm.

state can be divided into three parts, a linear part (0 – 35 V) a second part (35V – 65V) following the Pool – Frenkel relation [16]:

$$I = I_{0\exp} (V / V_0)^{1/2},$$

and a third part (65 V – V_{th}) where the current increases exponentially with the voltage according to [17]:

$$I = I_{0\exp} (V / V_0).$$

At a threshold voltage V_{th}, a switching process takes place after which further increase in the applied voltage causes the current to increase to the 'on' state as shown by part (bc) of plot A in Figure 2. Reducing the voltage to zero from its value in the 'on' state resulted in zero current (part co). Decreasing the film thickness to 275 nm results in decreasing V_{th} as shown in plot B of Figure 2. This result is in agreement with previous observation for different amorphous semiconductors [18, 19].

Figure 3 shows the variation in V_{th} with ageing time for the same sample of Figure 2-A after and before annealing at 328K for one hour. The threshold switching voltage decreases sharply during the first few days for both annealed and unannealed samples. After about two days, V_{th} starts to saturate. The value of V_{th} for the unannealed sample, however, was measured to be always higher than the corresponding value for the annealed films measured after the same ageing time. Similar behavior was obtained for the other thickness. Thus, we may conclude that either annealing or ageing for relatively long period may stabilize and improve switching properties.

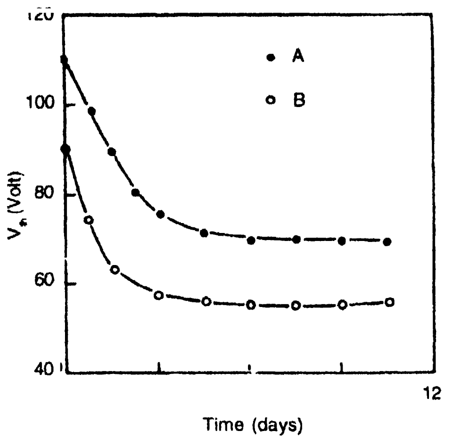

Figure 3. Variation in the threshold voltage V_{th} with ageing period for CuInSeS thin films of thickness 323 nm. (A) unannealed film. (B) film annealed at 328K.

Figure 4 shows the current – voltage characteristics for evaporated CuInSeS thin films of 323 nm thick, annealed at different annealing temperatures (303, 328, 353, 378, 398 and 423 K). The curves are characteristic of threshold switching where transformation from a high-resistance, off-state into a low-resistance, on-state takes place as the voltage exceeds a threshold value V_{th}. Moreover, annealing the films at different annealing temperature improves the characteristics and results in decreasing V_{th} as shown in Figure 4. Similar behavior was obtained for films of 275 nm thick as shown in Figure 5. This decrease will be shown later to be exponential.

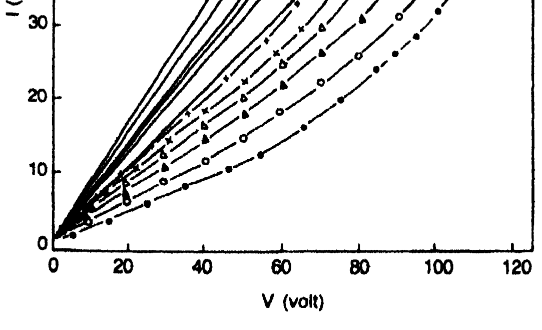

Figure 4. Current–voltage characteristics for as-deposited CuInSeS thin films of thickness 323 nm as a function of annealing temperature.

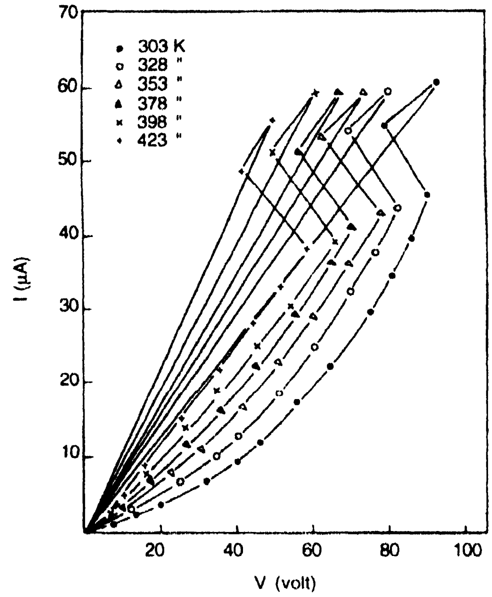

Figure 5. Current–voltage characteristics for as-deposited CuInSeS thin films of thickness 275 nm as a function of annealing temperature.

The dependence of the threshold voltage on the ambient temperature can be explained in terms of a thermal model in the pre-switching region. The conductivity process in semiconductor materials is well known to be of activated type. Therefore increasing the temperature of material in the Joale-heated regions provides a mechanism for the current to increase.

The calculated temperature dependence of V_{th} for CuInSeS thin films of thicknesses 323 nm and 275 nm are shown in Figures 6 and 7. From these figures it is clear that the V_{th} increases with

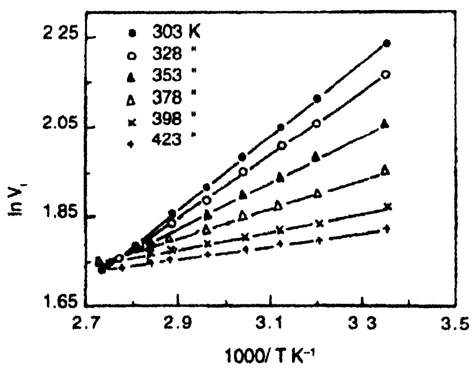

Figure 6. Logarithmic plot for switching threshold voltage V_{th} *versus* reciprocal temperature for as – deposited CuInSeS thin films of thickness 275 nm annealed at different annealing temperatures.

increasing the film thickness. The relation between log V_{th} *versus* 100/*T* are linear and can be put in the form (5):

$$V_{th} = V_0 \exp (E_s / KT),$$

where E_s is the threshold voltage activation energy.

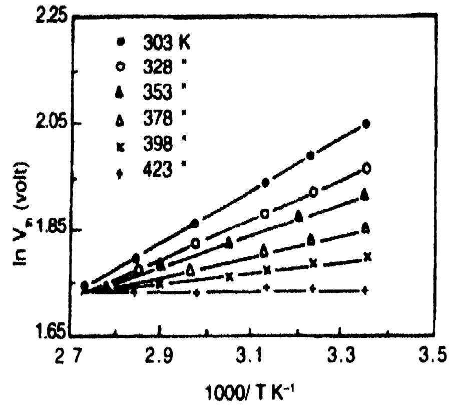

Figure 7. Logarithmic plot for switching threshold voltage V_{th} *versus* reciprocal temperature for as-deposited CuInSeS thin films of thickness 323 nm annealed at different annealing temperatures

The calculated values of E_s for CuInSeS thin films in comparison with the conductivity activation energy ΔE obtained from previous work [14], give the value of $E_s / \Delta E \cong 0.55$. This is in agreement with the observation of Shimakawa *et al* [20] for the thermal breakdown process. Moreover, the calculated values of V_{th} and E_s for sample of 323 nm thick, are plotted in Figure 8 *versus* the annealing temperature.

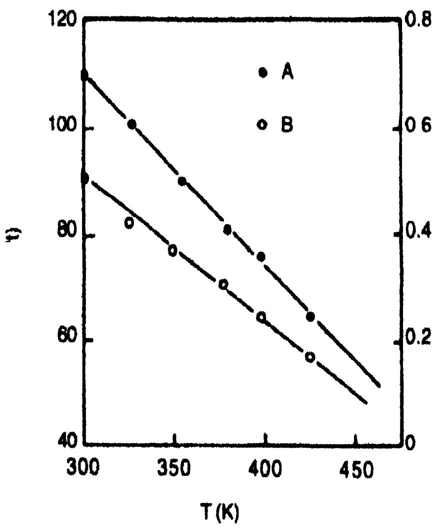

Figure 8. The threshold voltage V_{th} (line A) and the threshold voltage activation energy E_s (line B) for CuInSeS thin films of 323nm thick as a function of annealing temperature.

Both of the quantities decrease linearly on increasing annealing temperature.

4. Conclusion

Measurements of the current-voltage characteristics of both as-deposited and annealed films of amorphous CuInSeS thin films fit completely within the accepted picture of thermal breakdown. The annealing process and the decreasing of thickness improve the switching characteristics and decrease the threshold voltage V_{th}. Both the threshold switching voltage and threshold voltage activation energy E_s decrease linearly with increasing annealing temperature.

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